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CHARACTERIZATION OF NYLON 6 BY ^{15}N SOLID STATE NMR

by

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Submitted to

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Characterization of Nylon 6 by ^{15}N Solid State NMR

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ABSTRACT

The solid state ^{15}N NMR characterization of nylon 6 is reported. Nylon 6 (20% ^{15}N enriched) was prepared by anionic polymerization of isotopically enriched caprolactam. The samples were prepared by three different treatments: quenched from the melt, slowly cooled and annealed, and artificially plasticized with excess caprolactam. CP/MAS spectra of the ^{15}N enriched samples showed a single sharp peak (α crystal form) at 84.2 ppm (relative to glycine) and a broader resonance at 87.2 ppm. Relaxation experiments were conducted to determine $T_{1\text{N}}$, $T_{1\text{H}}$, and $T_{1\rho}$ for each sample at 300K. The crystalline resonance was found to have $T_{1\text{N}}$'s of 125-416s, consistent with crystalline nylon 6. The downfield peak had two measurable $T_{1\text{N}}$'s: a short component with T_1 of 1-3s and a second component with a longer T_1 of 19-29s. The two components for the non-crystalline peak are thought to belong to a liquid-like amorphous region and a more rigid "interphase" region lying between the crystalline and amorphous regions. $T_{1\rho}$ measurements were consistent with two-phase (crystalline plus amorphous) morphology although the two component decay for the amorphous region was not observed. The presence of plasticizer (caprolactam) tended to decrease $T_{1\rho}$ relaxation times which is consistent with lowered T_1 's. ^1H T_1 measurements were apparently dominated by spin diffusion that masked any differences between the regions.

The chemical shift anisotropy (CSA) of static samples are also shown. Motion in the amorphous region can be monitored by observing an isotropic peak at elevated temperatures. The effect of plasticizer (caprolactam) contributes to this motion. At temperatures above 100°C, the most deshielded (σ_{33}) component is lost from the CSA spectrum suggesting a previously unreported motion occurring in the rigid crystalline region. This motion is postulated to be associated with the intermolecular hydrogen bond between adjacent chains.



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Characterization of Nylon 6 by ^{15}N Solid State NMR

INTRODUCTION

High resolution solid state NMR is becoming an important tool for characterizing polymer systems. Cross polarization and magic angle spinning (CP/MAS) along with high power decoupling allow acquisition of high resolution spectra of natural abundance ^{13}C nuclei with good sensitivity. The ^{13}C solid state CP/MAS NMR of some important commercial polymers has improved our understanding of their microstructure and phase behavior.¹⁻⁵ Relaxation studies have identified non-crystalline regions poorly characterized by x-ray.³

Recently, we have demonstrated that solid state CP/MAS NMR of natural abundance ^{15}N is readily obtainable on solid polyamides.^{6,7} In addition, ^{15}N CP/MAS peaks were shown to correlate with the two predominant crystal forms found in most solid polyamides; i. e. namely α and γ crystal forms. Resonances were observed for other regions which could not be assigned to either crystal form. Further study by NMR and molecular modeling calculations showed nitrogen chemical shifts to be extremely sensitive to conformation about the amide group potentially providing a tool for observing ordered region conformations in solid polyamides.⁸

Although natural abundance spectra are attractive from a general utility point of view, the low sensitivity of nitrogen makes observation of small amounts of impurities and reaction byproducts difficult or impossible. Relaxation experiments (T_1 , $T_{1\rho}$) are also time consuming and may be impossible on most instruments with most samples. Our interest in examining the previously unobserved non-crystalline and amorphous regions in polyamides by ^{15}N CP/MAS prompted us to prepare an isotopically enriched polyamide sample.

We chose to prepare an ^{15}N enriched sample of nylon 6 because it is an important commercial polyamide which has been thoroughly characterized in the solid state by many techniques (DSC, IR, x-ray) including solid state ^{13}C NMR.^{4,5} Laboratory preparation of nylon 6 is relatively straight-forward. Isotopic enrichment was accomplished using commercially available hydroxylamine hydrochloride (99% ^{15}N) as shown in Figure 1. Here we report details of the polymer synthesis as well as ^{15}N NMR characterization of nylon 6 under a variety of conditions using several NMR methods.

EXPERIMENTAL SECTION

^{15}N NMR. Spectra were obtained on a Bruker MSL-200 NMR spectrometer operating at a field strength of 4.7 T and equipped with a Bruker MAS probe. The ^{15}N resonance frequency was 20.287 MHz and

that of the ^1H was 200.13 MHz. Samples were placed in fused zirconia rotors fitted with Kel-F caps and spun at 3.0 to 3.2 KHz with dry air. Crystalline glycine was placed in the rotor with the samples and used as an internal chemical shift reference (0 ppm). CP/MAS spectra were obtained with a standard crosspolarization pulse sequence using a $3.5\ \mu\text{s}$ ^1H 90° pulse and a mixing pulse of 2 ms. High power decoupling was used during a 50ms acquisition time with a nutating field of 62-68 KHz. Dipolar dephasing experiments were accomplished with the pulse sequence of Opella and Frey⁹ with a delay (T_D) of 20 to 100 μs .

^{15}N spin-lattice relaxation times (T_{1N}) were obtained using the CP-90- τ -90 pulse sequence developed by Torchia.¹⁰ Other relaxation measurements were obtained using the pulse sequences shown in Figure 2. Pulse sequence I (described previously³) is a ^1H 180- τ -90 inversion recovery experiment for measuring ^1H T_1 by monitoring the ^{15}N signal. $T_{1\rho}$ measurements were made using pulse sequence II. Pulse sequence III was used to obtain ^{15}N spectra without cross-polarization.³

Peak deconvolution of the overlapping crystalline and amorphous resonances in the CP/MAS spectrum was accomplished using TENSOR, a Bruker-supplied Pascal program for simulating overlapping NMR resonances as combinations of Lorentzian or Gaussian lineshapes. The chemical shift anisotropy of static ^{15}N spectra were simulated using POWDER, a Bruker Pascal program for simulating NMR lineshapes in solids. Both programs were run on an Aspect 3000 computer.

Polymer Synthesis. Cyclohexanone and polyphosphoric acid were obtained from Aldrich Chemical Co., Milwaukee, Wisconsin. ^{15}N labeled hydroxylamine hydrochloride (99% ^{15}N) was obtained from ICON Services, Inc., Summit, New Jersey. Solvents and other materials were reagent grade and used as received.

^{15}N Cyclohexanone Oxime: In a 10ml round bottom flask was placed 1g (0.014 mole) hydroxylamine hydrochloride (99% ^{15}N) and 1.5g (0.016 mole) cyclohexanone. To the reactants were added 5ml absolute ethanol and 5ml dry pyridine. The flask was purged with dry nitrogen, capped with a rubber septum, and placed in an oil bath at 80°C for 7 hours. The solution was then poured into a 50 ml beaker and the solvents evaporated under a stream of dry air. The remaining amber colored residue was triturated with ice cold water to precipitate the crystalline product. The crystals were filtered to yield 0.94g (59%) of crude cyclohexanone oxime melting at $86-90^\circ\text{C}$. (Note: The procedure above gave the oxime in 80% yield using unlabeled hydroxylamine hydrochloride reagent. Yields of the oxime were consistently lower when using the ^{15}N labeled hydroxylamine hydrochloride, presumably due to impurities present in the ^{15}N labeled reagent.)

^{15}N Caprolactam: Caprolactam (99% ^{15}N) was prepared by Beckmann rearrangement of the oxime using polyphosphoric acid in a procedure similar to one previously described.¹¹ Crude cyclohexanone oxime (400mg) was placed in a 25ml round bottom flask. Polyphosphoric acid (20g) was added to the flask and the

mixture gently heated over a low flame until the oxime dissolved. The flask was capped with a rubber septum and placed in an oil bath at 50-55 °C for 18 hours. The flask was removed from the bath and 10ml ice cold water was added with stirring. The aqueous mixture was poured into a 150 ml beaker and 2 or 3 drops of phenolphthalein indicator solution added. The acidic solution was titrated with 4N KOH until basic. The slightly basic solution was extracted with 4 50ml-portions of dichloromethane. The organic layers were combined and the dichloromethane evaporated in a stream of air to yield a white crystalline solid. The product was further purified by column chromatography (150 mesh basic alumina with a mobile phase of 5% v/v MeOH/CH₂Cl₂) to remove phenolphthalein. After evaporation of the solvents, the product was recrystallized from hot cyclohexane to give caprolactam-¹⁵N, m. p. 69-70 °C; yield 350mg (85%). The purified ¹⁵N labeled caprolactam was combined with unlabeled material to give approximately 20% ¹⁵N content. This material was used for polymerization reactions described below.

¹⁵N Nylon 6: Caprolactam (250mg at 20% ¹⁵N enrichment) was weighed into an oven dried glass vial. To this was added 3 µl N-acetylcaprolactam. The vial was placed in an oil bath at 160 °C and purged with a slow stream of dry nitrogen. Sodium hydride (10mg of a 60% dispersion in mineral oil) was added all at once to the molten solution. After about 30 seconds, the solution became opaque and viscous. The polymerization was continued for 5 minutes. The vial was then removed from the bath and allowed to cool. The vial was crushed and the solid nylon plug was recovered in quantitative yield. A portion of the crude reaction product was retained for further study. The remainder was extracted overnight with methanol and dried under vacuum at 80 °C.

The extracted samples were placed between sheets of aluminum foil coated with a fluoropolymer mold release agent, then melt-pressed at 250 °C and 20,000 psi to give films of approximately 0.3mm thickness. The molten samples were either quenched in ice-cold water or annealed in the press at 160°C for 2 hours. The percent crystallinity was determined by DSC measurement of the heat of fusion for each sample as previously described.¹²

RESULTS AND DISCUSSION

1. CP/MAS and T_{1ρ} of Crystalline and Amorphous Nylon 6.

The CP/MAS spectrum of nylon 6 is shown in Figure 3. Only 18,000 scans were required to obtain excellent signal-to-noise for this 100mg sample. The spectrum shown is similar to natural abundance ¹⁵N spectra we previously reported.^{6,7} The main strong peak clearly overlaps a broader resonance at lower field. The

overlapping peaks were fit with a composite lineshape (Figure 4) and the individual components deconvoluted as shown. From the deconvoluted components, the upfield resonance is located at 84.2 ppm with a linewidth at half height of 2.4 ppm. This peak was previously correlated with the α crystal form of nylon 6.^{6,7} The broader downfield resonance is centered at 87.2 ppm and possesses a linewidth at half height of 6.3 ppm. This resonance had not been observed in our previous work with polyamides at the ^{15}N natural abundance level. We believe this to be the signal from the non-crystalline or "amorphous" fraction of the nylon sample since its chemical shift appears midway between the α and γ resonances typically observed for nylon 6⁶ and other nylons⁷. (The γ form gives a sharp resonance at 88.5 ppm).⁶

To conclusively identify the downfield resonance as that of the amorphous region, relaxation experiments were conducted to evaluate the mobility of each region by monitoring spin-lattice relaxation times ($T_{1\text{N}}$). Using the method of Torchia¹⁰, relaxation times $T_{1\text{N}}$ were obtained at 300K for resonances at 84.2 ppm (α crystal resonance) and 87.2 ppm (approximate position of the amorphous resonance) for several samples. Figure 5 displays the ^{15}N spectra obtained with τ delays shown. The downfield "amorphous" resonance decays rapidly while the crystalline peak at 84.2 ppm remains strong after 40 seconds. Figure 6 shows a plot of magnetization decay for the crystalline component of the annealed sample. The crystalline component had a $T_{1\text{N}}$ of 416s. Figure 7 shows the two component decay of the amorphous fraction of the same sample with a $T_{1\text{N}}$ of 29.6s and an additional component with $T_{1\text{N}}$ of 1.9s. The two shorter T_1 's for the 87.2 ppm is consistent with an amorphous fraction with much greater mobility than the crystalline portion of the sample. In addition, the detection of two $T_{1\text{N}}$'s may indicate two types of amorphous regions: a bulk amorphous fraction with liquid-like mobility and a non-crystalline "interphase" region with restricted motion. Similar phase morphology is observed in polyethylene where the crystalline and the non-crystalline "interphase" region are clearly delineated by their $T_{1\text{C}}$ relaxation times.³ To our knowledge, this is the first report of NMR observation of an interphase region in a semicrystalline polyamide as well as the first relaxation measurements of crystalline and amorphous regions by ^{15}N CP/MAS.

^{15}N T_1 measurements are also reported in the Table for the in situ prepared sample as well as extracted samples that were quenched from the melt. The amorphous regions in all samples have shorter relaxation times than the crystalline regions, a fact consistent with ^{13}C relaxation studies of these materials.⁴ In addition, the in situ prepared samples have shorter $T_{1\text{N}}$ values than any of the methanol extracted samples. Since the $T_{1\text{N}}$ values are associated with motions of the polymers, a shorter $T_{1\text{N}}$ value for the in situ sample indicates more rapid motion, due either to plasticization by residual caprolactam in the sample or differences in the crystalline regions. Caprolactam has been shown to plasticize polyamides to improve flexibility and elongation.^{13,14}

Increased motion brought about by plasticization may account for the difference in relaxation times T_{1N} for the amorphous region. The increase in T_{1N} for the crystalline region of the unplasticized samples cannot be attributed to plasticizer effects. However, the process of extraction and heating of the sample may alter the size of crystalline domains. Spin lattice relaxation times of semicrystalline polymers have been shown to increase substantially with increasing crystal lamellar thickness.¹⁵ The increase in T_{1N} on annealing the sample is consistent with increasing crystal lamellae thickness.

We took advantage of the difference in spin lattice relaxation times T_{1N} between the two phases to directly observe the amorphous fraction. Using pulse sequence III shown in Figure 2, a MAS spectrum of the ^{15}N labeled nylon 6 was obtained without cross-polarization. By using a recycle delay of 5 to 10 seconds, the ^{15}N magnetization in the crystalline regions is quickly saturated. The nuclei in the amorphous region with shorter T_{1N} can then be observed directly. Using this method, the spectrum of the amorphous region was obtained (Figure 8, lower trace). This spectrum is nearly identical to the deconvoluted peak from the CP/MAS spectrum shown in Figure 4; i. e. the resonance is broad and downfield of the α crystal peak but upfield from the observed position of the γ crystal peak. Spectral subtraction gives the center trace in Figure 8. Now the resonance for the α crystal form is clearly seen as a symmetrical Lorentzian line with contributions from the non-crystalline region removed.

2. Static Cross Polarization Spectra (Chemical Shift Anisotropy)

The anisotropic chemical shifts (CSA) in solids can yield much information about the local electronic environment of a nucleus.¹⁶ Although tensor elements have been estimated from the powder spectra of a number of ^{15}N containing compounds,^{17,18} only one single-crystal ^{15}N study has been reported for an amide (glycylglycine) giving tensor orientations with respect to bond angles.¹⁹ We are aware of no previous reports in the literature describing ^{15}N chemical shift anisotropies of polyamides. This is not surprising since the random orientations of nuclei in semicrystalline polymers precludes absolute determination of tensor orientations with respect to the bond direction. Nevertheless, ^{13}C CSA spectra of polymers can be sensitive to motions in the solid state.²⁰ ^{15}N CSA spectra should be superior to ^{13}C for probing nylon 6 since only one chemically distinct nitrogen is present in the polyamide repeat unit.

A static ^{15}N spectrum of nylon 6 which has been extracted with methanol is shown in Figure 9, lower trace. The upper trace in Figure 9 shows the calculated CSA powder spectrum at 300K. From POWDER calculations the individual tensors of the anisotropy were calculated: $\sigma_{11}=5$ ppm; $\sigma_{22}=60$ ppm; $\sigma_{33}=180$ ppm. The calculated isotropic chemical shift (σ_{iso}) is 81.6 ppm, in good agreement with the value of 84.2 ppm obtained

through MAS.

The pattern shown in Figure 10, upper trace, is the *in situ* prepared sample at 350K, i. e. slightly above T_g . A peak with narrow linewidth is seen at approximately 87 ppm while the remainder of the spectrum is a typical pattern for a non-axial shielding tensor. The upper trace was obtained using the normal CP pulse sequence. The lower trace was obtained without CP by using pulse sequence III and a recycle delay of 7s. The crystalline components with long T_{1N} have become saturated in the lower spectrum with the resonance for the mobile fraction remaining. It was unclear whether the peak in the lower spectrum was due to the plasticized amorphous material or simply due to ^{15}N -labeled caprolactam still dissolved in the sample (which should be a liquid at this temperature). Plasticization was confirmed by taking the extracted nylon 6 and immersing it in molten (unlabeled) caprolactam at 120°C. Figure 11 shows the CSA spectra of plasticized and unplasticized nylon 6 at two different temperatures. It can be seen that the isotropic resonance is more intense for the plasticized sample at any given temperature. The narrowing of the isotropic peak on addition of plasticizer gives clear evidence that plasticization is increasing the motional freedom of the amorphous fraction. The powder pattern for the crystalline fraction remains virtually unchanged at these temperatures.

In an attempt to observe the amorphous fraction in the unplasticized static sample, ^{15}N CSA spectra were obtained at various temperatures as shown in Figure 12. At 27°C, the non-axial powder pattern is seen. As the temperature is increased, a narrow amorphous resonance appears centered near 84 ppm. This peak becomes more intense at higher temperatures and is clearly seen above 100°C. The chemical shift of the amorphous fraction (84.3 ppm) approaches the isotropic chemical shift obtained through MAS. Again, rapid motion has averaged the anisotropy of the amorphous fraction. However, higher temperatures are required to achieve the same motion that is observed in the plasticized nylon sample.

Another interesting phenomenon is observed in the CSA spectra of Figure 12. As the temperature is increased from 27°C to 100°C, the downfield component of the powder pattern σ_{33} becomes smaller. At 115°C this component is either no longer sharply defined or has disappeared altogether. Note also that the σ_{22} and σ_{11} elements remain essentially unchanged from the room temperature spectrum. This indicates a retention of non-axial symmetry since, in an axially symmetric pattern, the σ_{22} and σ_{11} elements should average to some intermediate value.¹⁸ Although the pattern remains non-axially symmetric, the loss of the σ_{33} component at elevated temperature suggests the onset of motion associated with some tensor component of the amide nitrogen.

Interestingly, the tensor element σ_{33} associated with this component has been shown to lie nearly parallel to the NH bond in amides.¹⁹ This suggests a change in intermolecular hydrogen bonding at elevated

temperatures. An infrared study of the effect of temperature on hydrogen bonding in amorphous nylons by Skrovanek and coworkers²¹ found that the amide groups remain nearly 100% hydrogen bonded at temperatures up to 210 °C. The average hydrogen bond strength, however, was shown to decrease. Frequency shifts and changes in absorptivity in the IR were attributed to relatively large vibrational displacements of the NH bond.²¹ In the crystalline region of the polyamide, the relatively small hydrogen will have the best chance for rapid motion even in the solid lattice. The concept of a "mobile" hydrogen that oscillates at a frequency sufficient to attenuate the σ_{33} component alone is consistent with the remaining crystalline components of the CSA spectrum at 150 °C.

This argument is further supported by dipolar dephasing experiments on the *in situ* prepared nylon 6 samples at 300K (Figure 13) and 350K (Figure 14). The upper trace in each experiment shows the normal CP/MAS result. The lower trace shows the dephasing due to dipolar coupling with a T_D of 100 μ s. The peak in Figure 11 is due only to molten caprolactam. After removing the caprolactam, only a small fraction of the signal remains. This indicates that strong dipolar coupling between ^{15}N and the attached ^1H returns to attenuate the signal.

At 370K (upper limit for MAS with our probe) the dipolar dephasing experiment (Figure 15) shows a small resonance remaining at T_D of 120 μ s. At this temperature, enough motion is present to weaken the dipolar interaction such that the signal is not completely lost. Note that the chemical shift does not change significantly throughout the experiment. The peak which remains may be argued to be part of the amorphous phase which now has more liquid-like mobility. Our relaxation experiments, however, confirm the remaining peak to be correlated with the α crystal form and not the amorphous region. The fact that significant motion can occur in the crystalline region to diminish the dipolar interaction tends to support the "mobile" proton model.

3. T_{1H} and Spin Diffusion

T_{1H} measurements were made using pulse sequence I at temperatures of 300K and 350K. The T_{1H} values were obtained by measuring the recovery of the ^{15}N magnetization at different τ . Since the ^{15}N resonances were already determined for the crystalline and amorphous components, the proton relaxation of each phase can be measured indirectly by observing the decay in ^{15}N magnetization as shown in Figure 16. The T_{1H} values of the *in situ* sample and the extracted sample are shown in the Table.

The ^1H T_1 values for each sample are about 1 second, very close to those for the crystalline region of polyethylene.³ Unlike polyethylene, which contains a very liquid-like amorphous region³ with a much shorter T_{1H} , the amorphous region of nylon 6 has very nearly the same T_{1H} . The fact that the two phases have very

different T_{1N} but similar T_{1H} indicates rapid ^1H spin diffusion between the phases. To confirm that the fast ^1H spin diffusion observed was not unique to the ^{15}N nucleus, the analogous relaxation experiment observing the ^{13}C nucleus was performed. ^{13}C resonances for the crystalline and amorphous regions (previously identified by Veeman⁴) were measured. Nearly identical T_{1H} values were obtained confirming the presence of rapid spin diffusion between phases.

4. $T_{1\rho}$ Measurements

$T_{1\rho}$ measurements were made using pulse sequence II and are reported in the Table. The crystalline region has the longer relaxation time (13-58 ms) and the amorphous region the shorter (0-40 ms). Although the increase in relaxation times $T_{1\rho}$ correlates with increasing percent crystallinity, the large differences in relaxation times seen for ^{15}N T_1 are not evident. The reason for this has been discussed by several authors studying semicrystalline polymers by ^{13}C CP/MAS.²²⁻²⁴ They point out that rotating frame relaxation ($T_{1\rho}$) is not pure spin-lattice in nature but has a considerable spin-spin component due to rapid ^1H spin diffusion between the different phases.²³ In highly crystalline systems, the rotating frame relaxation was found to be completely dominated by spin-spin relaxation.²⁴ In such systems, the $T_{1\rho}$ of the crystalline phase is usually shorter than the amorphous region because of more efficient T_2 in the crystalline region. In these nylon 6 samples, spin diffusion, although highly evident in the nearly identical T_{1H} values for both the crystalline and amorphous phases, does not dominate $T_{1\rho}$. Nevertheless, the two amorphous components seen in the T_{1N} relaxation experiment are not evident from $T_{1\rho}$ measurements.

Although information gained from the $T_{1\rho}$ experiment is somewhat limited by ^1H spin diffusion (in this case), the relative values for $T_{1\rho}$ may contain information about plasticization of the amorphous phase. ^{13}C $T_{1\rho}$ measurements of other polymers confirm that plasticizers act to increase molecular mobility and reduce the relaxation time.²⁵ Since the plasticizer occupies only the amorphous fraction, it should be possible to monitor the motion of the amorphous region by observing the $T_{1\rho}$ of the downfield non-crystalline resonance. Values reported in the Table for $T_{1\rho}$ of the amorphous as well as the crystalline regions show shorter values for the plasticized in situ prepared sample than for the extracted sample. The amorphous peak for the plasticized sample decayed so rapidly into the noise level of the spectrum that accurate determination of $T_{1\rho}$ for this peak was not possible. Once the plasticizer is removed, the $T_{1\rho}$ increases substantially. Similar to the T_{1N} data, the increase in $T_{1\rho}$ of the **crystalline** component may be related less to plasticizer effects and more to changing crystallite size.

CONCLUSIONS

The ^{15}N labeled nylon 6 sample was prepared in good yield by anionic polymerization of the labeled caprolactam monomer. Enrichment of approximately 20% ^{15}N has allowed direct $T_{1\text{N}}$ and $T_{1\rho}$ relaxation measurements as well as $T_{1\text{H}}$ determination by indirect observation of ^{15}N cross polarization.

As expected, the rigid crystalline region has a much longer $T_{1\text{N}}$ relaxation than the more mobile amorphous region. The $T_{1\text{N}}$ of the crystalline fraction was 111-416s. Two components were observed in the relaxation of the amorphous peak: a fast component with T_1 of 1-3s and a longer component with T_1 of 19-29s. The two non-crystalline components are thought to belong to amorphous and non-crystalline "interphase" regions, respectively.

Less dramatic behavior is seen in $T_{1\rho}$ relaxation times. Only a single amorphous component could be observed. This anomaly is attributed to considerable ^1H spin-spin relaxation within the sample resulting in similar $T_{1\rho}$ values. This conclusion is further supported by ^1H T_1 relaxation experiments which show that rapid ^1H spin diffusion is occurring between the phases. Addition of plasticizers, which concentrate in the amorphous region, decrease the observed $T_{1\rho}$ of the both the crystalline and amorphous regions. However, the effect on the crystalline $T_{1\rho}$ may be better attributed to differences in crystallite size than to increased motion.

The first chemical shift anisotropy patterns of a polyamide have been obtained on nylon 6. The CSA powder patterns show the growth of an amorphous signal at elevated temperatures with a chemical shift near the isotropic value obtained with MAS. The addition of plasticizer (caprolactam) causes this signal to grow in at lower temperatures confirming that plasticization is increasing molecular mobility in the amorphous region. The σ_{33} component becomes less prominent with increasing temperature and finally disappears above 115°C. The source of this component has not been previously reported, but is speculated to be motion associated with the tensor component along the NH bond of the amide group. Specifically, we assign this motion to rigid vibrational libration of the hydrogen atoms in the still hydrogen-bonded crystalline portion of the sample.

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TABLE

<u>Sample</u>	<u>% xtal</u>	<u>Parameter</u>	<u>Amorphous Phase (87.2 ppm)</u>		<u>Crystalline Phase (84.2 ppm)</u>
In situ	23	T1N	-----a	26s	111.5s
		T1H		0.99s	0.95s
		T1ρ		-----b	13.8ms
Melt Quenched	29	T1N	2.7s	19s	230s
		T1H		1.06s	1.03s
		T1ρ		24.3ms	44.5ms
Annealed (160 oC)	45	T1N	1.9s	29.1s	416s
		T1H		0.75s	0.78s
		T1ρ		37.9ms	57.7ms

aShort T1 component was not observed for this sample.

bDecayed too rapidly to be observed.

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LIST OF FIGURES

Figure 1. Reaction scheme for preparation of ^{15}N enriched nylon 6.

Figure 2. Pulse sequences used in this paper.

Figure 3. ^{15}N CP/MAS spectrum (18,000 FID's) of ^{15}N enriched nylon 6 showing α crystal form (large peak at approximately 84 ppm) and broader, overlapping region downfield (non-crystalline region).

Figure 4. TENSOR fit of the ^{15}N CP/MAS lineshape of nylon 6. The bottom traces show the calculated fit along with the individual components.

Figure 5. ^{15}N spectra obtained from the CPT_1 pulse sequence of Torchia with τ delays shown. The lower trace ($\tau = 40\text{s}$) shows mainly the crystalline component with long $T_{1\rho}$.

Figure 6. ^{15}N Spin-lattice relaxation of nylon 6. Plot of intensity of ^{15}N resonance at 84.2 ppm versus τ along with single exponential fit used to determine T_1 .

Figure 7. ^{15}N Spin-lattice relaxation of nylon 6. Plot of intensity of ^{15}N resonance at 87.2 ppm versus τ . The bi-exponential fit is plotted along with individual T_1 components showing two-component decay.

Figure 8. ^{15}N MAS spectra of nylon 6 at 300K. Upper trace: Spectrum with cross-polarization; main peak for α crystal form is seen along with overlapping resonance downfield. Lower trace: ^{15}N spectrum obtained using pulse sequence III (recycle delay of 5s) showing only the noncrystalline region with shorter $T_{1\rho}$. Center trace: Spectral subtraction of upper and lower traces showing the symmetrical resonance line for the α crystal form of nylon 6.

Figure 9. Static ^{15}N CSA spectrum of methanol extracted sample at 300K. Upper trace is the best fit from POWDER showing the relative positions of the tensor components.

Figure 10. Static ^{15}N NMR spectrum of in situ prepared nylon 6 at 350K. Top trace: CP spectrum showing both crystalline and non-crystalline components. Bottom trace: Spectrum obtained with a 90° pulse and decoupling showing non-crystalline components.

Figure 11. ^{15}N CSA powder spectra of nylon 6. Left column: Methanol extracted samples (unplasticized) by caprolactam; Right column: Samples plasticized by heating in molten caprolactam.

Figure 12. Static ^{15}N NMR spectrum of annealed nylon 6 sample obtained with cross polarization and high power decoupling at different temperatures. The non-crystalline component at approximately 84 ppm becomes increasingly sharper at elevated temperatures.

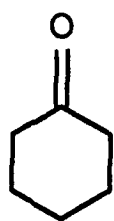
Figure 13. ^{15}N dipolar dephasing spectrum of in situ prepared nylon 6 at 300K. Upper trace: $T_\rho = 20$ micro-

seconds with magnetization intact. Lower trace: $T_D = 100$ microseconds with rigid components dephased.

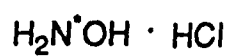
Figure 14. ^{15}N dipolar dephasing of in situ prepared nylon 6 at 350K. Upper trace: $T_D = 20$ microseconds. Lower trace: $T_D = 100$ microseconds showing mobile regions due to molten caprolactam.

Figure 15. ^{15}N dipolar dephasing experiment at 370K of methanol washed sample. Note the resonance at 84 ppm for $T_D = 120 \mu\text{s}$ is not completely dephased indicating onset of rapid motion in or near the crystalline region.

Figure 16. Stack plot of CP/MAS spectra obtained with pulse sequence I using τ delays shown. The trace with $\tau = 1\text{s}$ shows equivalent inversion of crystalline and amorphous ^{15}N resonances. This indicates protons associated with both the crystalline and amorphous regions have equivalent T_{1H} .

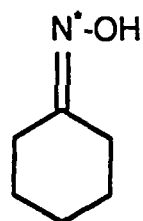


+



EtOH/Py

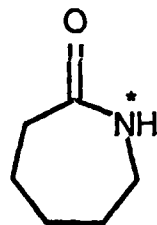
reflux



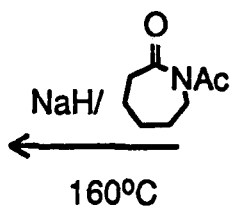
80%

polyphosphoric
acid

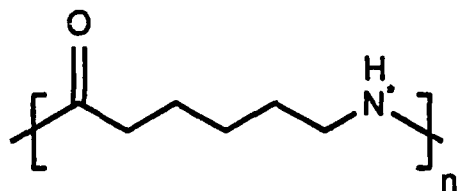
40°C / 18 Hrs.

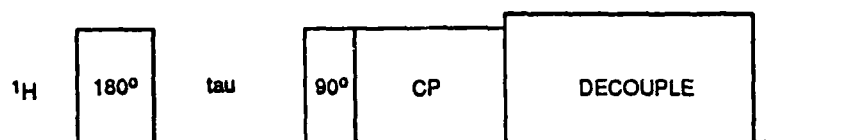


85%

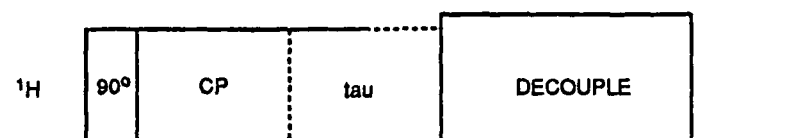
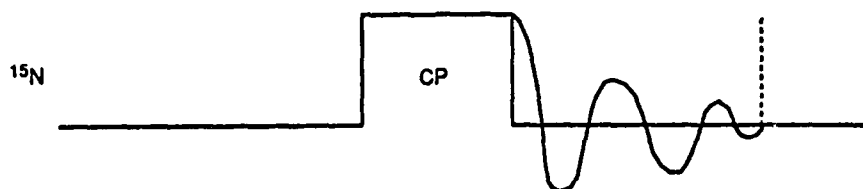


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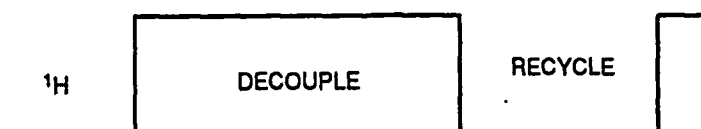
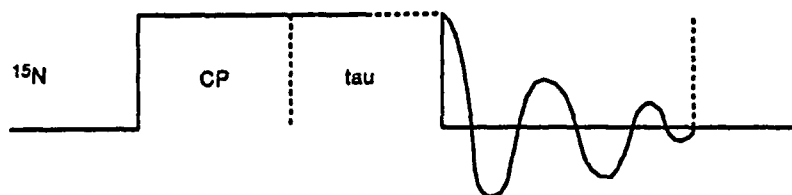




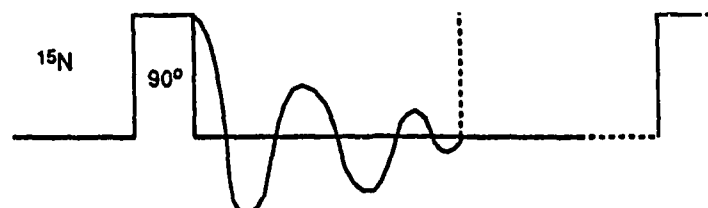
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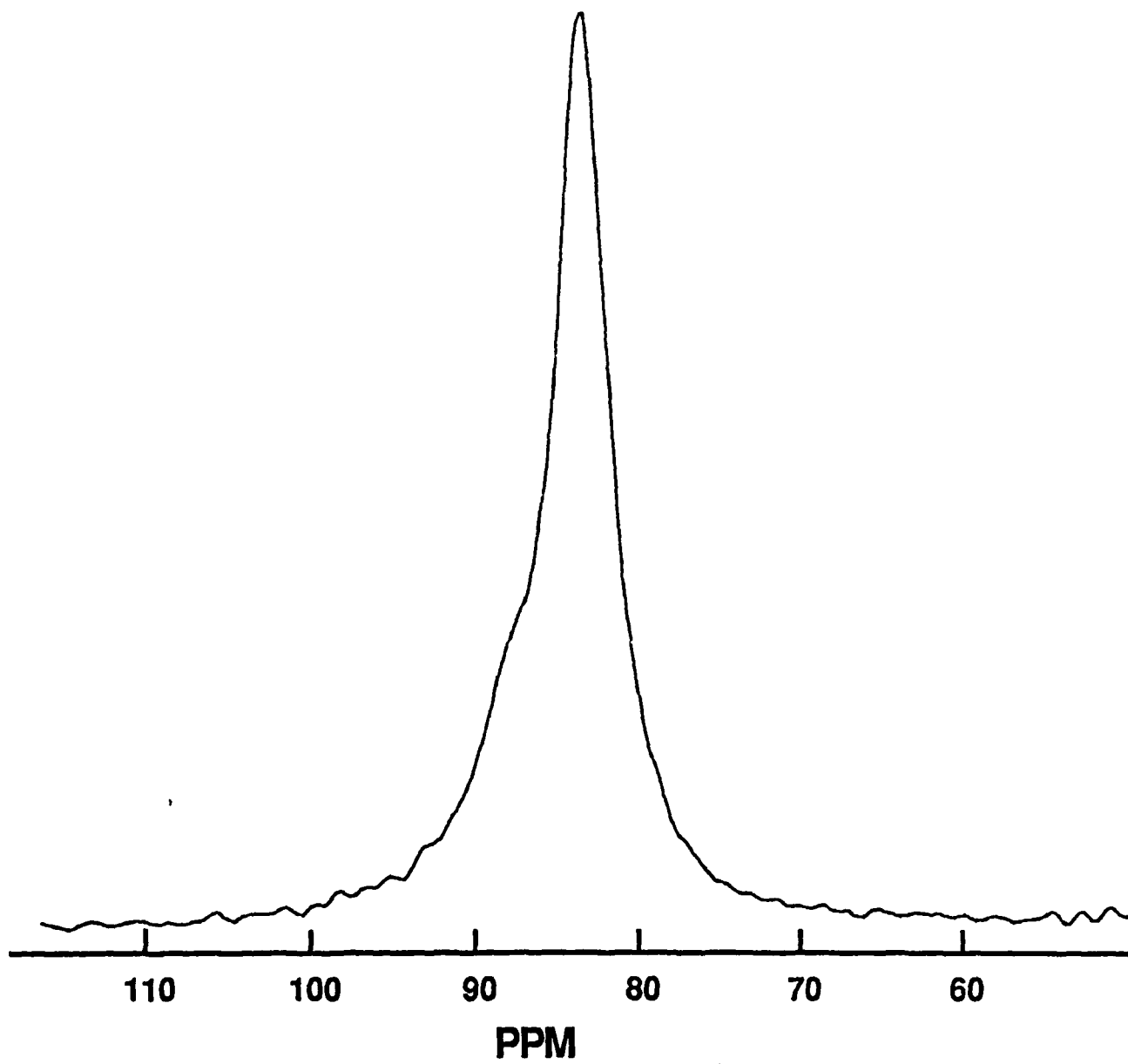


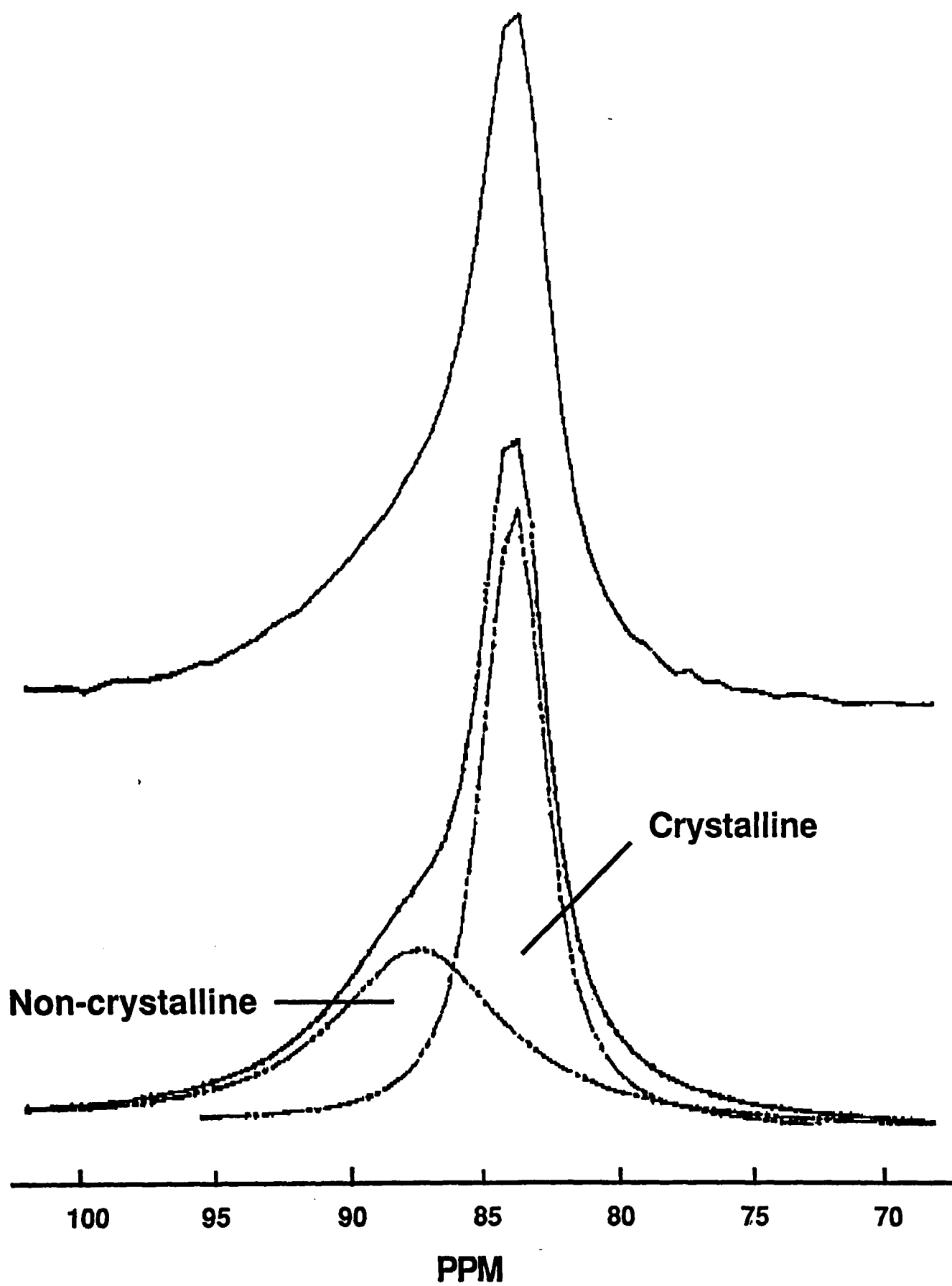
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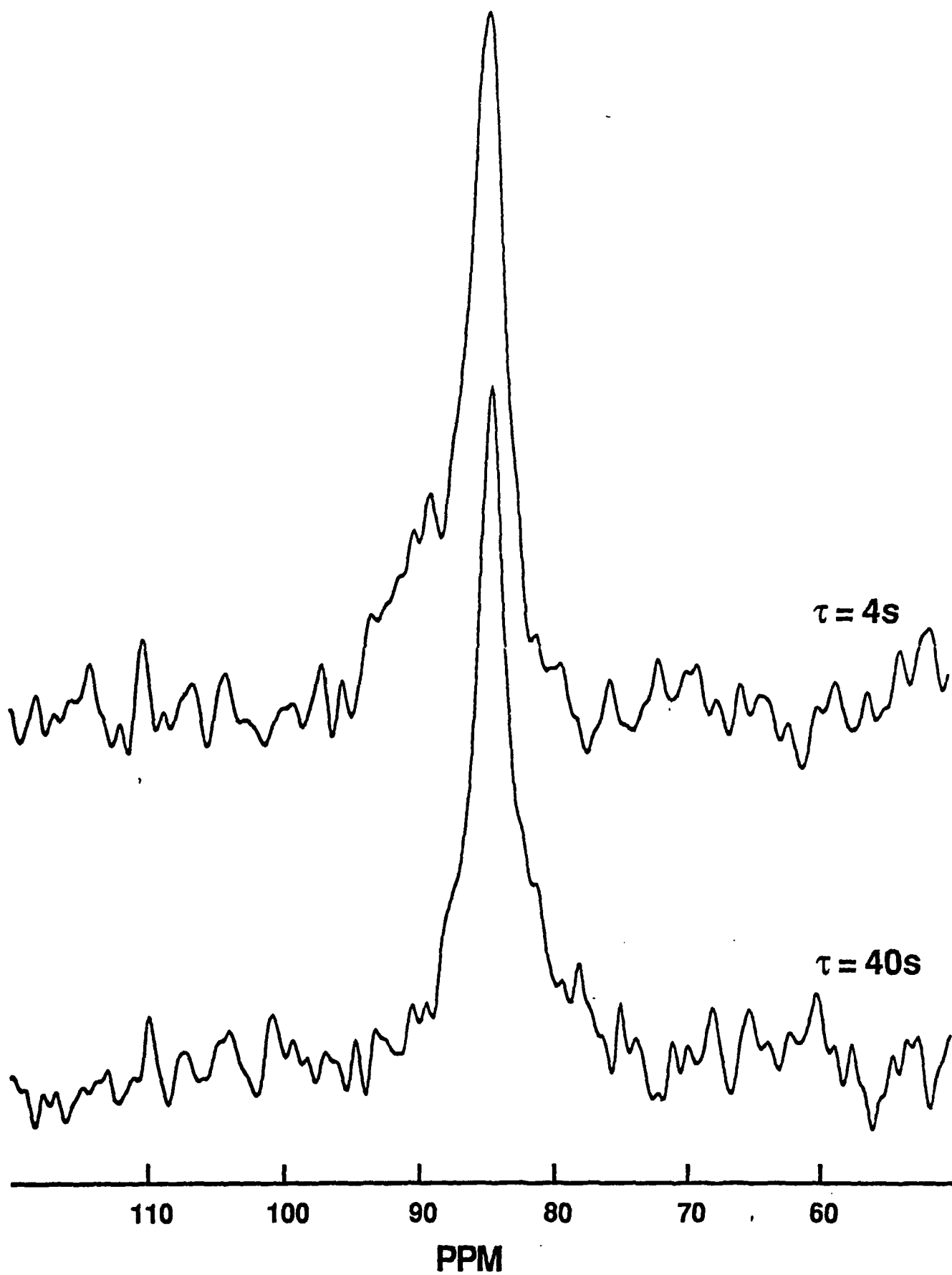


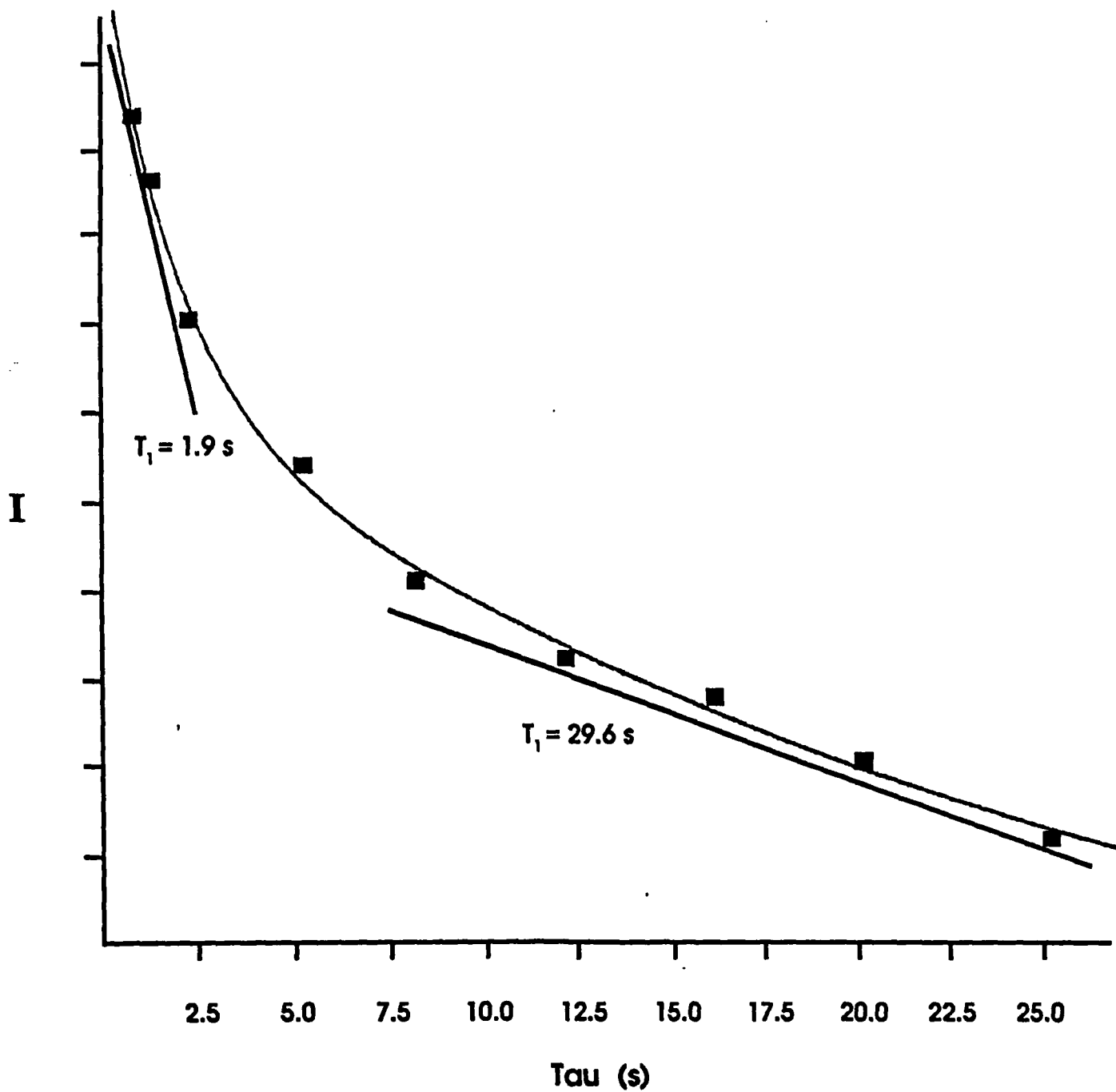
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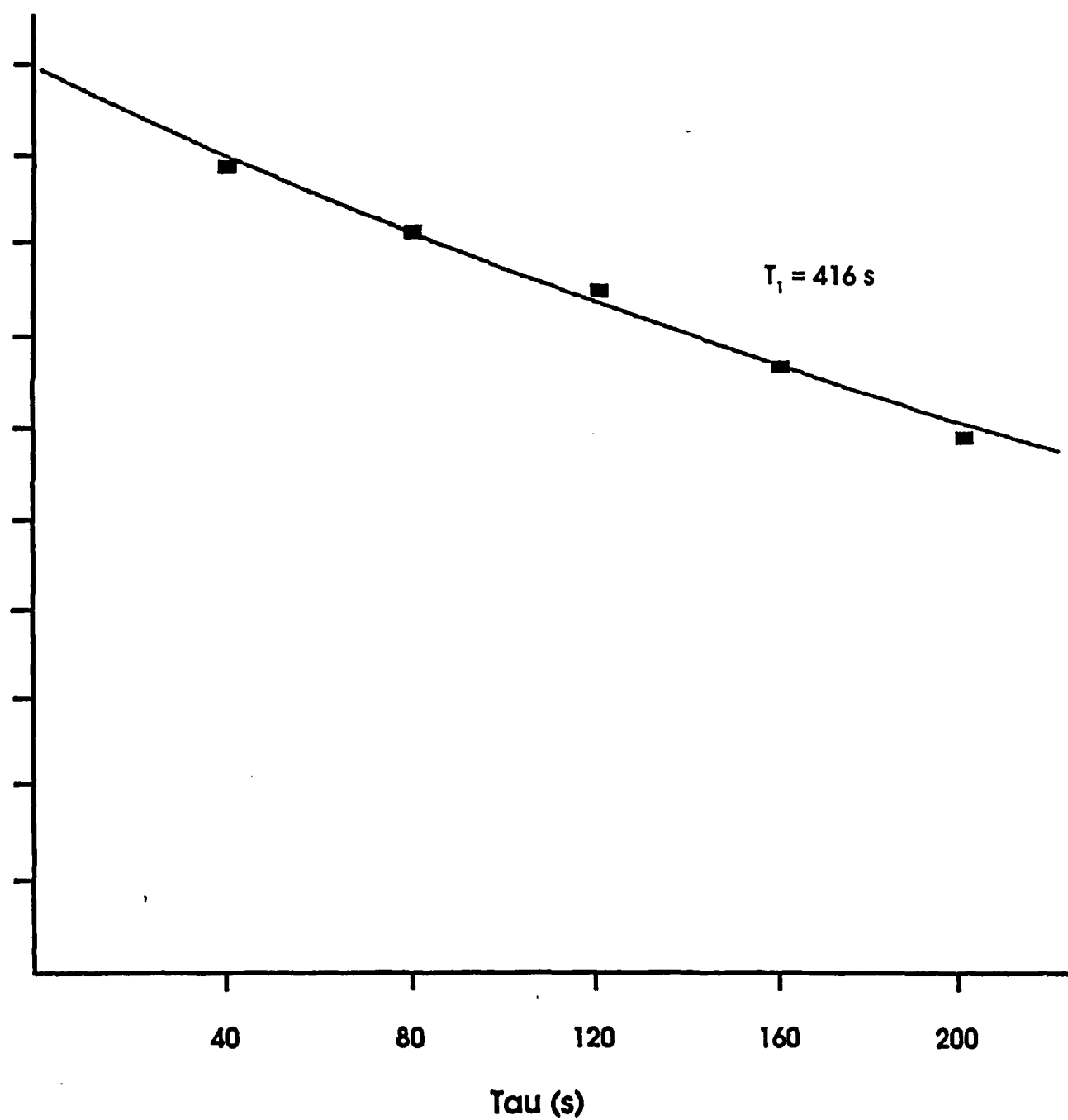


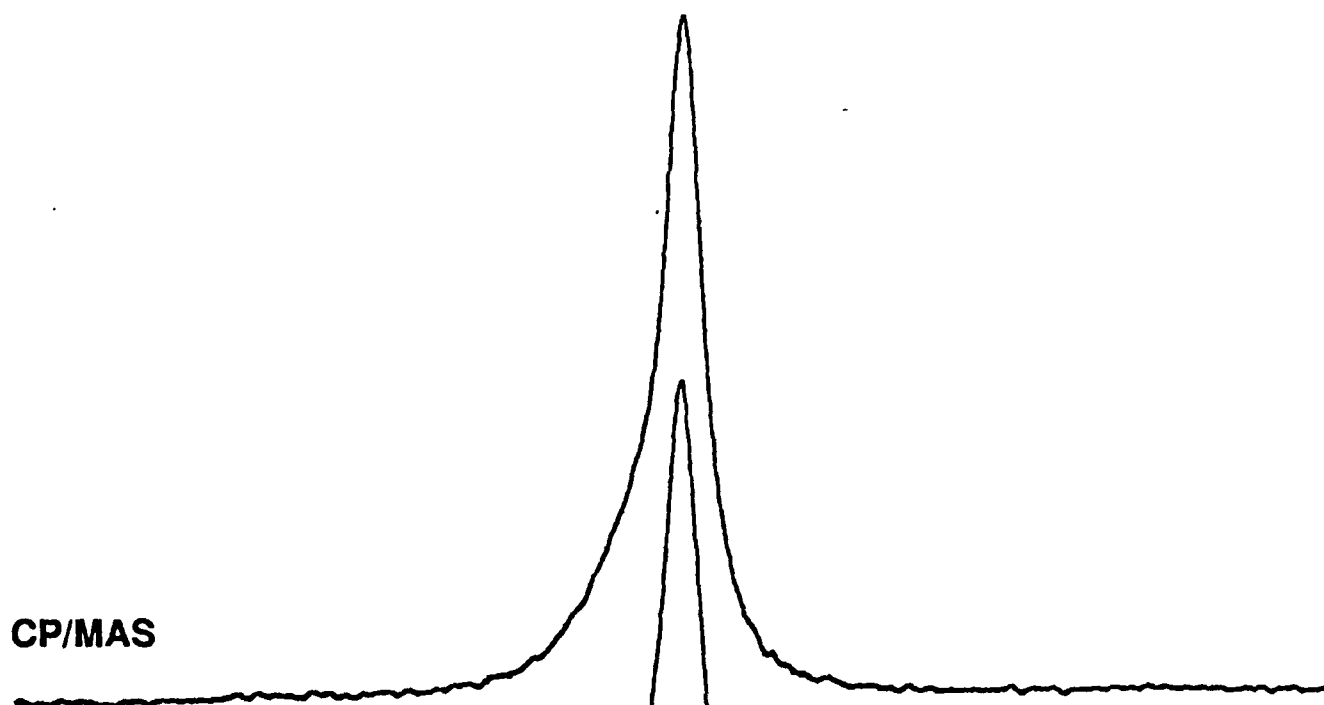






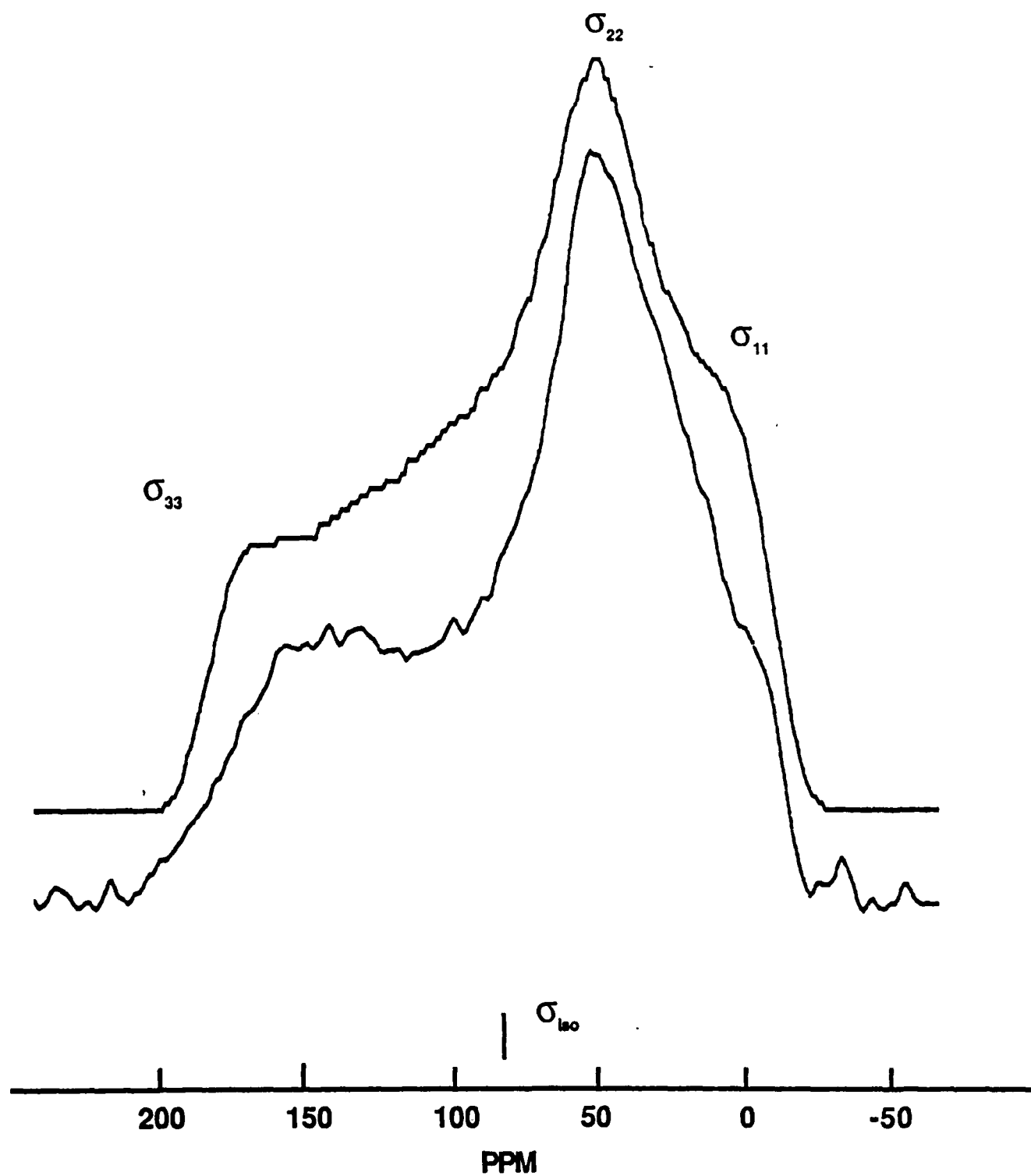
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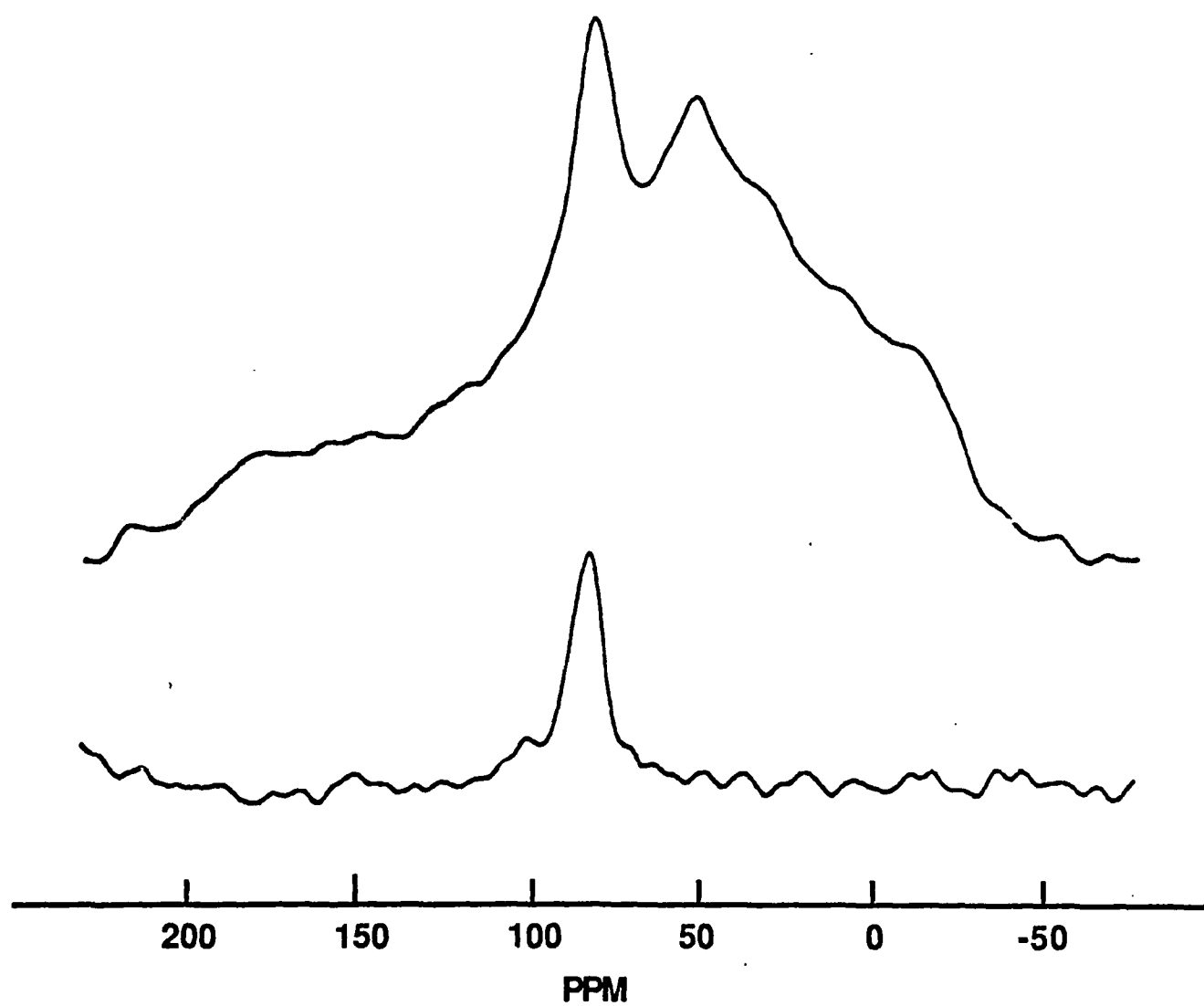


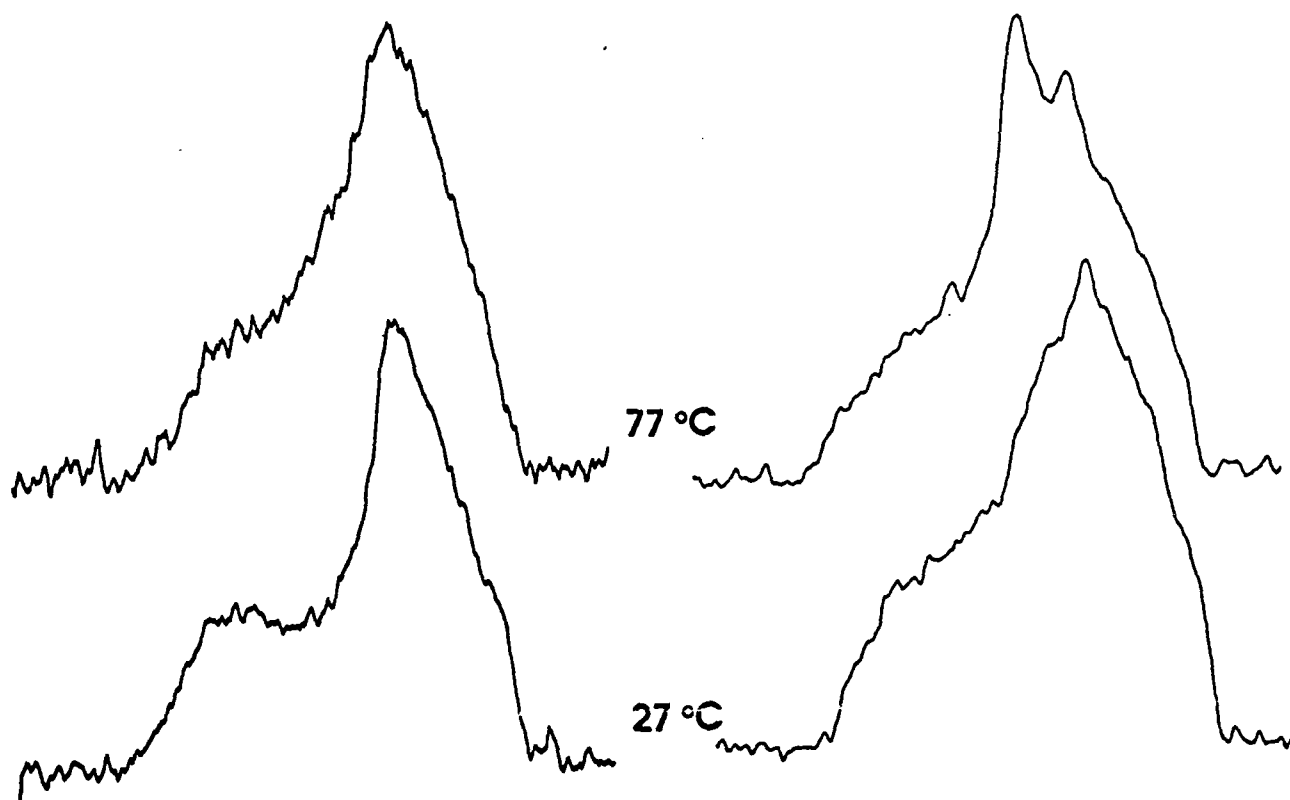


120 110 100 90 80 70 60 50

PPM







Unplasticized

Plasticized

